

CATALYTIC REACTOR FOR IMPROVED CARBON MONOXIDE CONTROL WITHIN THE HYDROGEN FEED STREAM OF A PEM FUEL CELL

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INTRODUCTION

The proton exchange membrane (PEM) fuel cell is considered a promising energy conversion device, based on environmental and energy efficiency advantages.¹ Even though hydrogen-air PEM fuel cell systems have been considerably improved over the past two decades, direct hydrogen systems present challenges for wide-spread automotive applications.² The advantage of contemporary fuel cells becomes compromised if their deployment requires a new complicated hydrogen infrastructure. On-board reforming of contemporary clean fuels is an alternative approach for supplying hydrogen for these PEM fuel cell vehicles. Fuels for such clean vehicles include natural gas, reformulated gasoline, alcohols, ethers and other hydrocarbons.³ Chemical conversion of these fuels using either partial oxidation or steam reforming generates a hydrogen stream diluted with carbon dioxide, nitrogen, steam and various contaminants including carbon monoxide. In the presence of CO stack efficiency is compromised, so fuel processing hardware must include features to manage impurities. The Fuel Cell Engineering Team at Los Alamos has pioneered successful approaches for gas cleanup. The effort combines catalyst development with novel reactor designs, perhaps suitable for future automotive applications. These large-scale experiments are supported by micro-scale investigations of catalyst performance. One important focus is to develop new approaches useful for achieving transient behavior of contemporary passenger vehicles. Such a gas clean-up device is termed a PROX (preferential oxidation) converter, even though oxidation is but one of the several reactions necessary for successful fuel cell system hardware.⁴

EXPERIMENTAL

Both micro-scale and larger (50-kW) device experiments are described. The micro-scale test stand permits catalyst evaluation using test gas mixtures selected to replicate operation with a variety of fuels, such as might result using a "multifuel reformer". For instance a simulated gasoline reformat might consist of 36% H₂, 17% CO₂, 28% N₂ and 17% H₂O. Small quantities of contaminants are added to such mixtures and then the mixtures are blended with controlled quantity of air. The resulting mixture is transferred to a volume of catalyst. Analytical tools including gas chromatography and gas chromatography mass spectrometry evaluate catalyst effectiveness. Considerable attention is paid to the fluid dynamics of the experiments to assure uniform gas composition, inlet temperature and laminar flow. These reactors can be either adiabatic ("hot spot") or isothermal, depending upon test conditions. The micro-scale reactor is used to determine performance data on a variety of catalyst types and to investigate techniques for effective control of other contaminants such as NH₃ or H₂S.

The large scale experiments replicate conditions used for microscale testing. One PROX reactor with three series, adiabatic sections is shown in Figure 1. Each section incorporates features to homogenize the gas mixture, to control entrance temperature and to assure laminar flow into the catalyst volume. Heat flow is primarily through convective processes. The overall large-scale design includes features designed to meet safety standards for hydrogen operation and to permit convenient exchange of catalyst samples and alteration of other internal features. The large experiment also permits dynamic measurement of gas composition and temperature within the catalyst volume to measure either "down the channel" or spatial (radial) data. Such information has proven very useful to confirm modeling predictions.

Experiments are computer controlled. The electronic systems sets appropriate reactant flows and controls temperatures and pressure. Importantly the data system also continuously evaluates for experimental faults such as hydrogen leaks and acts to terminate tests when certain release rates are reached.

RESULTS

Preferential oxidation depends upon rapid CO oxidation even in the presence of far larger mole fractions of hydrogen. The intent is to remove the CO with only small concurrent hydrogen oxidation. Although there have been significant improvements in anode fuel cell catalysts to increase CO tolerance, most contemporary systems dictate that inlet CO concentration should be set at below 30 ppm.

The removal rate of CO through oxidation on a platinum catalyst in the micro-scale reactor depends on the reaction temperature, as shown in Figure 2. The highest conversion of CO, or the lowest outlet CO concentration, is attained at 220°C and by further increase in reaction temperature leads to high outlet CO concentration. Additional experimental results support that increased CO found at temperatures exceeding 220°C is attributed to the rapid hydrogen oxidation at these temperatures which depletes oxygen and concurrent production of CO by the reverse shift reaction.

The inlet oxygen concentration was varied as shown in Figure 3 and the effect on CO control was measured. The outlet CO concentration was determined at 220°C and 260°C, respectively. At both reactions temperatures, oxygen is rapidly depleted by reaction with CO and H₂ at oxygen stoichiometry as high as to 3.0 based on the CO concentration. In this case a stoichiometry value of 1.0 is defined, for example, when the number of moles of oxygen is 0.5 that of the moles of CO—for example 250 ppm of oxygen, as a constituent of air, is added to a stream containing 500 ppm of CO. From Figure 3, an increase in oxygen stoichiometry at 220°C is found to be effective in reducing outlet CO concentration, while concurrent hydrogen loss is significant with the increase in oxygen stoichiometry at 260°C.

Figure 4 shows PROX device performance as a function of overall oxygen stoichiometry, summed for each of the stages based on the inlet CO content. Figure 4 shows results for an inlet concentration of 20,000, using three stages. The device output ranges from a CO concentration of 45 ppm to well below 20 ppm, depending upon conditions. In general these hydrogen-mixture cleanup devices perform as designed over a wide range of flow rates and inlet carbon monoxide concentrations.

Transient performance, CO control during a rapid change in either CO concentration or flow rate, can be achieved by either precise control of reactant flows or through intelligent catalyst design, or by a combination of these approaches. Transient performance at the 50-kW flow level during an event when a normal 8,000 ppm CO flow stream is changed to a 12,000 ppm CO gas stream. With appropriate alteration of the air injection rate, the device shows no performance degradation.

Other contaminants than carbon monoxide are troublesome. Some compounds will not influence PROX performance but can degrade stack performance. Others tend to poison the catalyst surfaces contained in the PROX device. The hydrogen generators also, at times, generate colloidal carbon ("soot"), a contaminant that can adversely influence PROX performance.

CONCLUSIONS

Gas cleanup-technology is an essential operation in on-board fuel processing systems. Today transportation fuel specifications are being adjusted to meet increasingly demanding environmental emission regulations. Cleaner fuels, especially low sulfur fuels, are more easily processed as hydrogen sources. New fuels, such as dimethyl ether, dimethoxy methane and gas-to-liquid ("Fischer Tropsch") compounds are additional steps along the pathway towards very clean vehicles. All of these clean fuels are also attractive candidates for fuel cell vehicles.

Although there has been considerable progress in gas clean-up technology, challenges remain. Such devices must address automotive applications with special requirements for low initial cost, ruggedness and reliability. Transients are also challenging, especially the transient during start-up of the vehicle. In these experiments the gases are

added to the catalyst at a temperature exceeding the "light-off" temperature. Special designs will be necessary to initiate operation within the 20 seconds, or so requirement, following a cold-soak period. Even so, much of the necessary technical design challenges for these devices have been successfully demonstrated.

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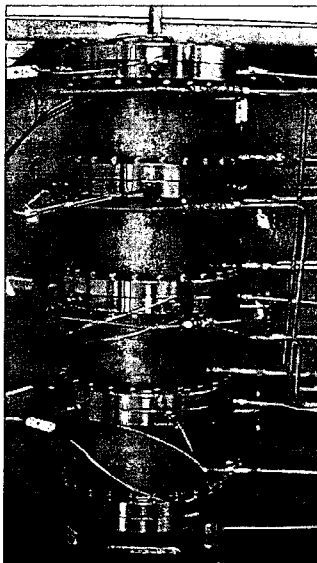


Fig. 1 The 50kW modular PROX assembled at the PROX test facility.

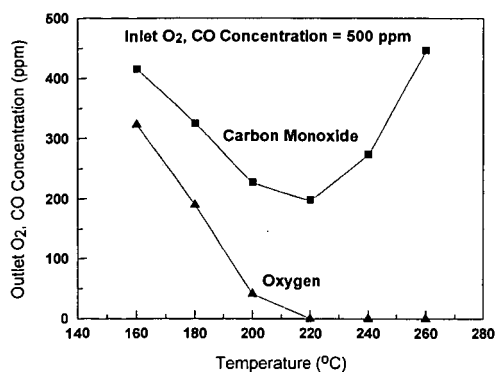


Fig. 2 The measured outlet oxygen and carbon monoxide concentrations with reaction temperature.

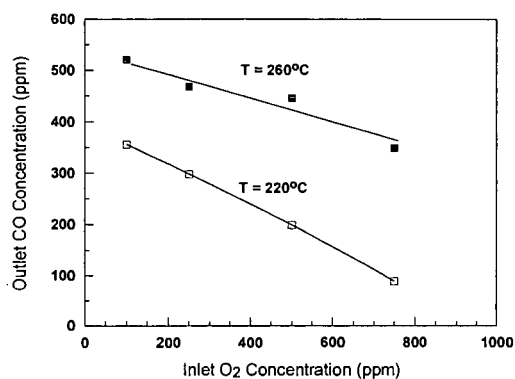


Fig. 3 The measured outlet carbon monoxide concentration as a function of inlet oxygen concentration.

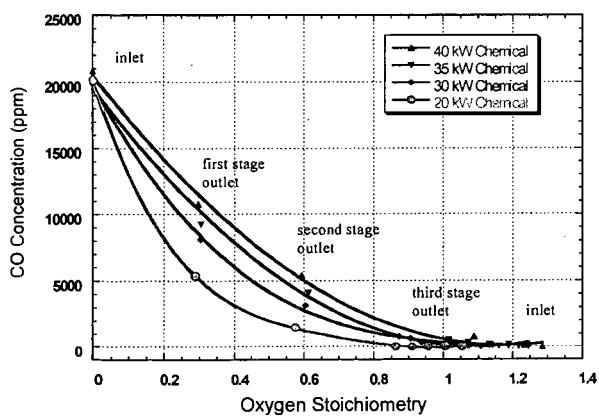


Fig. 4 PROX device performance as a function of overall oxygen stoichiometry.